Enhanced Power Stability for Proton Conducting Solid Oxides Fuel Cells

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Objectives

- Develop modified electrolytes that exhibit both high proton conductivity and excellent chemical and mechanical stability. Doped $BaZrO_3$ has been selected as basic materials for further modification.
- Develop a fundamental understanding of the mechanisms and barriers of proton transport in a proton ceramic fuel cell (PC-FC).
- Develop highly efficient electrocatalysts for the anodes and cathodes of PC-FCs based on the above-mentioned relatively new electrolytes.
- Develop rapid synthesis methodologies for both candidate electrolytes and candidate electrodes (or electrocatalysts).

Key Milestones

- Obtained the equation of state (EOS) of $BaZrO_3$.
- Calculated equilibrium proton positions in $BaZr_{1-x}Y_xH_xO_3$ with different dopant concentrations.
- Calculated preliminary reaction barriers for doped $BaZr_{1-x}Y_xH_xO_3$.
- Synthesized $BaZr_{1-x}Y_xO_{3-\delta}$ (x = 0.2, 0.3, 0.4, 0.5) by a modified Pechini process.

Approach

A key hurdle to the commercialization of solid oxide fuel cells (SOFCs) is their high cost, which, in part, is due to their high operating temperatures (800 to 1000 °C) and associated restrictions on materials choices. Recognition of this challenge has led the SOFC research community to search for alternatives to the standard SOFC electrolyte, yttria-stabilized zirconia that will enable reduced temperature operation (500 to 700 °C). One of the most promising alternatives is the familyof proton conducting perovskites that include $BaZrO_3$, $BaCeO_3$, and $SrCeO_3$ [1].

The current paradigm of focusing on empirical design of new materials for fuel cells (which requires expensive and time consuming projects to integrate these materials into devices in order to test the new materials) is inadequate to make the progress required over the next few years. Thus, we have developed an alternative approach in which newly developed first principles and computational methods are used in conjunction with experimental methods to develop optimized next generation PC-FC component materials. Follow-up experiments will be used to validate the computational predictions. By dedicating the expensive experimental efforts to the most promising systems, more time can be spent trying to optimize each system.

Our current quantum mechanical (QM) calculations are based on density functional theory (DFT) using generalized gradient approximation (GGA) to treat the exchange-correlation energy functional [2]. In these calculations, pseudopotentials are used to replace the

core electrons. All calculations are performed at T = 0K. The calculations use 3D periodic boundary conditions. The QM calculations are carried out using SeqQuest, in joint development between Sandia National Laboratories (Dr. Peter Schultz), and Caltech.

For application to large scale systems, the results from the QM calculations will be used to determine a reactive force field (ReaxFF) that can be used for thousands of atoms.

All oxides of interest in this project are synthesized using the Pechini method [4], in which metal nitrates are dissolved into an aqueous solution containing ethylene glycol and an acid, such as citric acid. We then identify the phase and composition using X-ray powder diffraction (to determine variations in the lattice parameters).

Results

QM calculations on $BaZrO_3$ and $BaZr_{1-x}Y_xH_xO_3$

Behavior of the energy, as a function of the volume, has been studied for cubic $BaZrO_3$ as well as stability of the equilibrium state against deformations at the constant volume. It was confirmed that the cubic phase is the most stable one, as suggested both experimentally and from previous theoretical calculations. Figure 1 shows the results of the QM calculations for the cubic phase of $BaZrO_3$ and a corresponding fit, according to the Rose EOS.

$$E(r_{ws}) = \Delta E(f_0^* - f_1^* a^* + f_2^* a^{*2} + f_3^* a^{*3})e^{(-a^*)},$$

where $a^* = (r_{ws} - r_{wse})/(r_{wse}\lambda)$, r_{ws} is the radius of the Wigner-Seitz sphere, r_{wse} is the equilibrium radius, and λ is a length scale. From the least square fit of the ab initio data, the following values for the free parameters were obtained: $\Delta E = 36.9076 +/- 0.0003$, $r_{wse} = 4.2441 +/- 0.0002$, $\lambda = 0.2438 +/- 0.0002$, $f_3^* = 0.1093 +/- 0.0013$. The bulk modulus,

$$B = -V\frac{dP}{dV} = V\left(\frac{d^2E}{dV^2}\right),$$

resulted from our calculations is 144.597 GPa, which is in good agreement with reported experimental values.

We also calculated energies of the system with different proton positions localized on edges of the YO_6 and ZrO_6 octahedra. This allows us to determine the equilibrium positions of the protons in $BaZr_{1-x}Y_xH_xO_3$ with different dopant concentrations (x = 0.125, 0.25 and 0.5), as well as to start analyzing the free energy barriers for proton transport along relevant trajectories

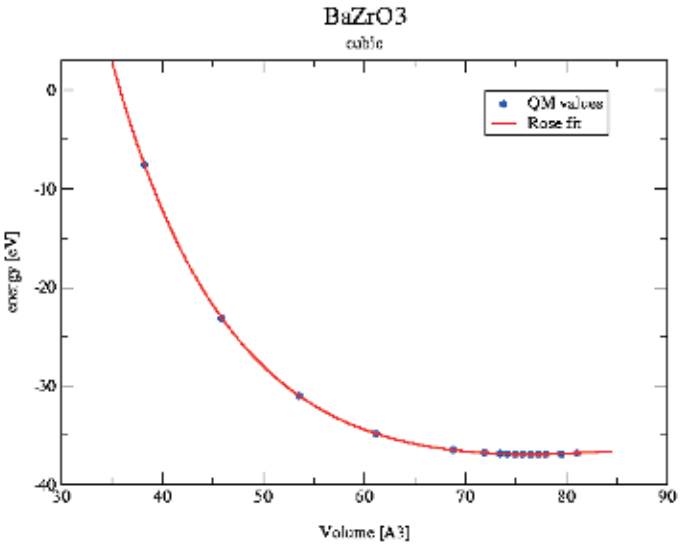

Figure 1. *Results of QM calculations (the full circles) for the cubic phase of $BaZrO_3$. The line shows the fit to the Rose EOS.*

in the structure (see Figure 2).

Synthesis and Phase Identification of $BaZr_{1-x}Y_xO_{3-\delta}$

$BaZr_{1-x}Y_xO_{3-\delta}$ (x = 0.2, 0.3, 0.4, 0.5) was synthesized by a modified Pechini route [4]. The precursors were $Ba(NO_3)_2$, $Y(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot xH_2O$ (x was determined by thermogravimetric analysis to be 1.96). EDTA and EG were used as polymerization/complexation agents at molar ratios of EDTA/ΣMetal = 2.0 and EDTA/EG=1/3. The powders derived were calcined at 1250 °C for 10 hours. X-ray diffraction (XRD) patterns of the samples were collected by a Philips X'pert Pro diffractometer using CuKa radiation.

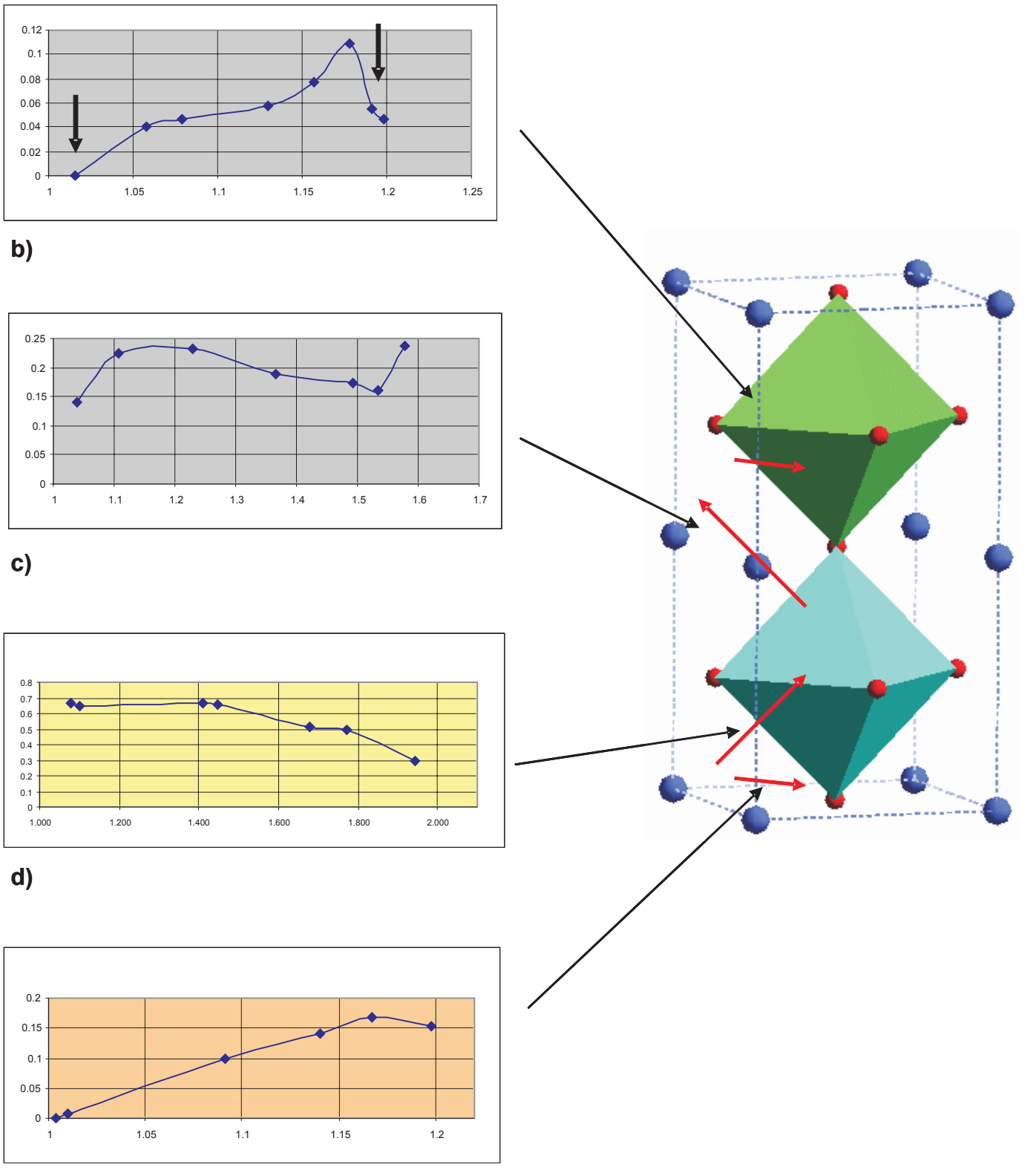

Figure 2. *Dependence of the energy (eV) on proton positions [the distance (Å) from the corresponding oxygen]. The arrows in the graphs point out the equilibrium proton positions. The energies are given with respect to the absolute minimum (Figure 2a). In Figures 2a and 2d, due to the symmetry of the system, the resulting energy is shown up to a half way between neighboring protons. In the figure of the atomic structure Ba atoms are denoted by blue balls, O atoms – red balls, ZrO_6 octahedron is light blue and YO_6 octahedron is green.*

Figure 3 shows the XRD patterns of the powders calcined at 1250 °C for 10 hours. The XRD patterns indicate that a single perovskite phase is formed in $BaZr_{1-x}Y_xO_{3-\delta}$ (x = 0.2-0.5). The peaks shift to the lower 2θ with increasing x, which could be explained by the ion size difference between Y^{3+}(0.892Å) and Zr^{4+}(0.72 Å). Therefore, the modified Pechini method can successfully be used for the synthesis of the proton conducting $BaZr_{1-x}Y_xO_{3-\delta}$ solid oxides with a wide range of the dopant concentration.

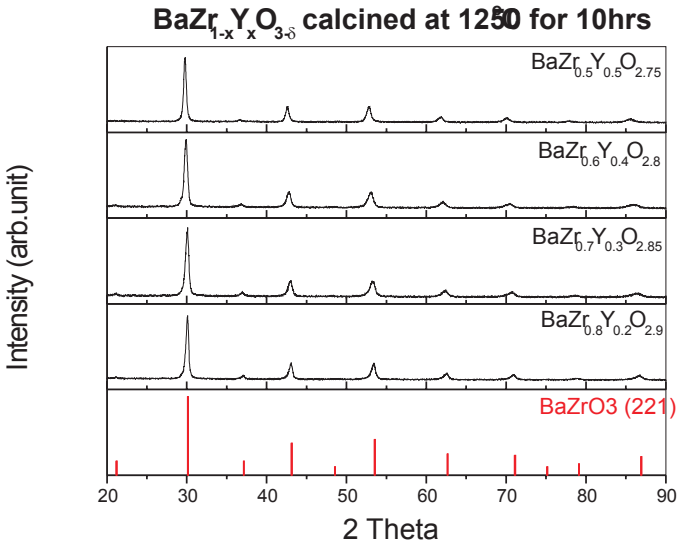

Figure 3. *X-ray diffraction patterns of $BaZr_{1-x}Y_xO_{3-d}$ powders calcined at 1250°C for 10 hours.*

Conclusions

Ab initio calculations of the EOS for BaZrO3 have been performed, and the bulk modulus has been obtained. The value of the modulus is in good agreement with reported experimental values. Equilibrium proton positions in Y-doped BaZrO3 with different dopant concentrations have been investigated. The general features of these positions confirm the result of the previous calculations. The high concentration of the dopant might lead to a trapping of the protons. The first estimation of the transition barriers has been performed, and the equilibrium positions of the protons have been determined. Usefulness of the modified Pechini process for the synthesis of the proton conducting solid oxides of interest in this project has been demonstrated. This synthesis route is particularly useful for obtaining homogeneous compositions and for reducing sintering temperatures. Future activities will include further study of the energy landscape, development of reactive force fields, based on ab initio QM calculations, mesoscale simulations of proton diffusion, and catalytic reactions.

References

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